

THE VAPOR PRESSURE OF SMALL DROPS*

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Gibbs did not consider the Kelvin equation for the vapor pressure of small drops for the obvious reason that it does not constitute chemical equilibrium. The Kelvin equation represents true equilibrium between vapor and a flat surface of liquid water, where the liquid is under a pressure greater than the vapor by any assigned value ΔP . For example, in a closed vessel in the presence of an inert, slightly soluble gas such as air a definite equilibrium exists which will be re-established if displaced by the transfer of water from the liquid phase to the vapor or vice versa.

For equilibrium between vapor and small drops as described by the Kelvin equation this is no longer the case. For a given partial pressure of vapor a drop must be of a particular radius. A drop which is slightly larger will grow by condensation, and a drop which is slightly smaller will evaporate. The situation does not even correspond to unstable equilibrium, since it does not satisfy the condition $\Delta F = 0$ so far as free surface energy is concerned. Gibbs¹ pointed out that the production of a drop of the required size from the vapor in the Kelvin equilibrium required an increase in free energy equal to one-third the surface free energy. The vapor in quasi-equilibrium with the drop has an additional free energy per mole $2 \gamma V^\circ/r$, where γ is the surface tension and r is the drop radius. But the free surface energy of a mole of water in the form of drops is $3 \gamma V^\circ/r$, as will be shown later. Incidentally, *free* surface energy can only be of significance when the equilibrium involves the creation or disappearance of surface. This only happens when the liquid phase is subdivided into small drops.

The equilibrium between a vapor and small drops is not a simple affair. Provided that the drops do not exceed a certain size, such an equilibrium is possible; but it necessarily involves a whole gamut of drop sizes and concentrations. Fortunately, we need consider only one particular drop size at a time in discussing the equilibrium. We shall proceed to discuss the range of conditions under which such equilibrium can exist. Before actually formulating the equilibria involved, it is necessary to consider the special thermodynamic properties which are possessed by small drops.

Surface Energy.—The first of these is the free surface energy, which, expressed in ergs per square centimeter, is the surface tension. This is ordinarily assumed to be independent of drop radius, but this cannot be true down to the point where the radius becomes that of a single molecule and the drop vanishes. This problem has been considered first by Gibbs and later by Tolman² and others, but no definite conclusions can be reached. What we are concerned with is not the validity of surface tension as a physical concept but rather the decrease in the free surface energy of the drop as the radius is decreased. From thermodynamics,

$$\gamma = \left(\frac{\partial H}{\partial \sigma} \right)_{T, P} - T \left(\frac{\partial S}{\partial \sigma} \right)_{T, P}, \quad (1)$$

where σ is the surface area in square centimeters. The first term on the right is larger than $T(\partial S/\partial \sigma)_{T,P}$ and will presumably always be larger, so that we can confine our attention to it. Stefan, following Laplace's theory of surface tension, concluded that, if the center of an atom or molecule was in the surface, the particle had lost one-half its neighbors and, therefore, that the enthalpy change in bringing a particle to the surface would be one-half the enthalpy of vaporization. This seemed to be a naive point of view, but the values for mercury are in fair agreement with Stefan's theory. In the case of associated liquids, the surface enthalpy is very much smaller than one-half the enthalpy of vaporization, which leads to the conclusion that the molecules are able to maintain hydrogen bonding even in a curved surface, and there seems to be no reason to assume an appreciable increase in surface enthalpy so long as the drop contains one hundred or more molecules. Since the co-ordination number in the liquid is probably five at a maximum, this will not be seriously constrained until the radius becomes very small.

While the second term of the right-hand side of equation (1) must always be exceeded by the enthalpy term, there is another contribution to the entropy of small drops to be taken into account, viz., the entropy of the drop considered as a gas molecule. There is no corresponding enthalpy term to be considered, and this term must become the overriding factor leading to stabilization as the drops approach molecular dimensions.

Effect of Drop Concentration.—Equilibrium in gaseous systems depends upon the partial pressures or concentration of the various species present. This dependence upon concentration comes in through the dependence, mentioned above, of the entropy of the drop, considered as a gas molecule, upon the concentration. Liquid water may be considered as having the classical number of degrees of freedom per molecule which contribute to its enthalpy and entropy. In the liquid drop, however, considered as a gas molecule, three of these degrees of freedom must be assigned to translation and three to rotation of the drop as a whole, and these contribute more to the entropy than does the average degree of freedom. The contribution of the free surface energy to the free energy per mole of the liquid drop varies inversely as the radius of the drop and becomes negligible in 1μ . The contribution of the entropy of the drop qua gas molecule diminishes as the inverse cube of the radius, and, while this contribution depends upon the concentration, all these terms become negligible at 1μ radius. For practical purposes, therefore, drops of 1μ radius may be considered as a continuous liquid phase with a normal vapor pressure. In addition to the contribution to the absolute entropy, the translational degrees of freedom involve the concentration of the drops through the term $-R \ln P_n$, where P_n is the partial pressure of the drops considered as gas molecules. This comes about because of the Bose-Einstein statistics which must be applied.

Spontaneous Nucleation.—As a result of these considerations, we may postulate a given concentration for any of the possible drop sizes in equilibrium with the vapor at any temperature and pressure. So long as the vapor is unsaturated, the concentration of the larger drop sizes is vanishingly small; but it is enormously sensitive to changes in vapor pressure, and at some point of supersaturation the drop concentration becomes finite at all radii. Another way of expressing this phenomenon is as a rate process. At vanishingly low concentrations the time required

for growth to finite (i.e., observable) size is infinite; a slight increase in supersaturation will shorten this time to a matter of seconds.

Kinetics of the Condensation Process.—Since all kinetic processes in gases at moderate pressures must be assumed to be bimolecular, we may consider the growth of the drop or cluster as a molecule by molecule condensation:

$$X_n + X = X_{n+1}, \quad \frac{P_{n+1}}{P_n} = Kp.$$

For purposes of calculation, however, it is convenient to consider the equilibrium

$$X_n = nX, \quad \frac{p^n}{P_n} = K_n. \quad (2)$$

If we write the equilibrium

$$X_{n+1} = (n+1)X, \quad \frac{p^{n+1}}{P_{n+1}} = K_{n+1}, \quad (3)$$

then we see that these three types of equilibria are consistent and derivable from each other. Subtracting equations (3) from equations (2), we have

$$X_n + X = X_{n+1}, \quad \frac{K_n}{K_{n+1}} = Kp. \quad (4)$$

Equilibrium between Cluster and Vapor.—Using the term "cluster" to designate the drop of diminishing size, let us write the equation for the equilibrium between the cluster of n drops and vapor,

$$\frac{1}{n} X_n = X, \quad \frac{p}{P_n^{1/n}} = K. \quad (5)$$

This equation, as written, is on the basis of one mole (18 gm.) of water, and the corresponding free energies will be so calculated. Using the prime for the cluster and the double prime for the vapor, we have for the chemical potentials

$$\begin{aligned} \mu' &= F_n^\circ + RT \ln P_n, \\ \mu'' &= F_r^\circ + RT \ln p. \end{aligned}$$

For the gaseous equilibrium

$$\frac{1}{n} \mu' = \mu'',$$

and

$$F_n^\circ = F_i^\circ + \frac{3 \gamma V^\circ}{r} + \frac{1}{n} TS'^\circ \quad (6)$$

Here V° is 18 cm.³, and $3 \gamma V^\circ/r$ represents the free surface energy (ergs) of 18 cm.³ of liquid water in the form of drops of radius r , S'° is the excess entropy of 1 mole of clusters considered as gas over that of liquid water, and n is the number of molecules per cluster.

If we remember now that $\ln p_0''$, the saturation pressure of water, is given by the equation

$$\ln p_0 = \frac{-\Delta F^\circ}{RT} = -\frac{F_V^\circ - F_L^\circ}{RT}, \quad (7)$$

where F_V° is the free energy of water vapor at the temperature T and 1 atmosphere, assuming ideal-gas behavior, and F_L° is the free energy per mole of liquid water likewise under standard conditions, we may write, from equations (5),

$$-RT \ln K = -RT \ln \frac{p''}{p_0''} = F_V^\circ - F_L^\circ - \frac{3 \gamma V^\circ}{r} + \frac{1}{n} TS'^\circ$$

or

$$\ln \frac{p''}{p_0''} = \frac{3 \gamma V^\circ}{rRT} - \frac{S - R \ln P_n}{nR} \quad (8)$$

Comparison with Experiment.—According to data in the current literature, air saturated with water vapor at 25° C. will, on cooling to -10° C. by adiabatic expansion, show evidence of spontaneous nucleation. We shall accordingly calculate the terms in equation (8) for these conditions. For the surface-energy term we shall assume $T = 263^\circ$, $\gamma = 75$ ergs/cm, and the volume of the water molecule 30×10^{-24} cm.

The surface-energy term becomes

$$\frac{9.6}{\sqrt[3]{n}}.$$

For the entropy term we have the following expressions from Paul:³

$$S_{tr} = 26.0 + (3/2)R \ln M,$$

where M is the molecular weight of the drop ($= 18n$).

$$\begin{aligned} S_{rot} &= 284.6 + (3/2)R \ln I, \\ I &= (2/5)mr^2 \quad (m = \text{mass of drop}). \end{aligned}$$

Assuming a symmetric number of 1, radius of 10 Å, and 133 molecules per drop, one calculates

$$S_{tr} = 49.0, \quad S_{rot} = 36.0.$$

It remains to calculate the value of $R \ln P_n$, which must be expressed in atmospheres. A concentration of 10^7 drops per cubic centimeter would correspond to $P_n = 10^{-12}$ atmospheres; hence

$$R \ln 10^{-12} = 55.9 \text{ E.U.}$$

10^7 nuclei should certainly produce a visible fog. A smaller concentration might suffice.

These assumptions give, for the total entropy term, 140 E.U. These values, therefore, lead to the equation

$$\ln \frac{p}{p_0} = \frac{9.6}{\sqrt[3]{n}} - \frac{70}{n}. \quad (9)$$

This equation gives a maximum at $n = 102$, and tables of calculated values are given herewith (Tables 1 and 2). The data are also plotted in Figure 1. The value $\ln(p/p_0) = 1.37$ at the maximum corresponds approximately to the fourfold degree of supersaturation that has been frequently reported in the literature.

TABLE 1

CALCULATIONS OF SUPERSATURATION FROM EQUATION

| n | $\sqrt[3]{n}$ | $9.6/\sqrt[3]{n}$ | $70/n$ | $\ln(p/p_0)$ |
|-----|---------------|-------------------|--------|--------------|
| 64 | 4 | 2.4 | 1.1 | 1.30 |
| 102 | 4.68 | 2.06 | 0.69 | 1.37 |
| 125 | 5 | 1.92 | 0.56 | 1.36 |
| 216 | 6 | 1.60 | 0.32 | 1.28 |

TABLE 2

VALUES OF P_n FOR
 $\ln(p/p_0) = 1.37$

| n | P_n (Molecules/Cm) |
|-----|-------------------------|
| 64 | $>10^9$ |
| 102 | 10^7 |
| 125 | $>10^8$ |

It is believed that the surface-energy term cannot be in serious error so long as the critical drop size contains more than one hundred molecules. The entropy term may be in error, but it is almost certainly too small. While an increase of several units would increase the critical drop size calculated, the effect is not very great because n is a divisor in the term. The maximum as calculated in Table 1 is very flat, but this is somewhat misleading. If one solves equation (8) for $\ln P_n$, using the value for the supersaturation $\ln(p/p_0) = 1.37$, one obtains a sharp minimum at $n = 102$. Thus $n = 102$ is the critical drop size as defined for spontaneous nucleation. Drops of this size exist at smaller concentration at equilibrium than drops of larger or smaller size. The equilibrium concentration is enormously sensitive to the degree of supersaturation.

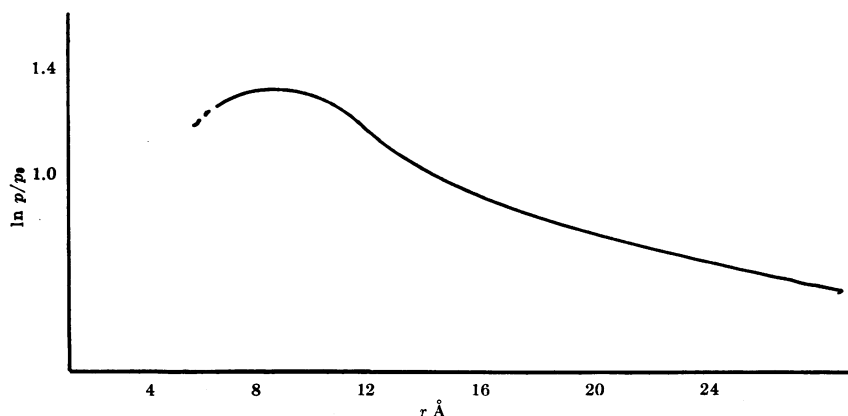


FIG. 1.—Logarithm of supersaturation plotted against radius in angstroms.

No attempt has been made in this paper to consider the rate of growth of drops or to give a critical review of data as reported in the literature. These questions will be considered in another paper which will give an account of some experimental attempts to produce spontaneous nucleation.

It should be obvious that the thermodynamic method used here can be applied to spontaneous nucleation in any sort of phase transition—for example, crystallization from a supersaturated solution. The entropy term is always manageable, but one must seek some sort of experimental approach to the estimation of interfacial energy.

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¹ J. W. Gibbs, *Collected Works* (New York: Longmans, Green & Co., 1928).

² R. C. Tolman, *J. Chem. Phys.*, **16**, 758, 1948.

³ M. A. Paul, *Principles of Chemical Thermodynamics* (New York: McGraw-Hill Book Co., 1951), p. 665.

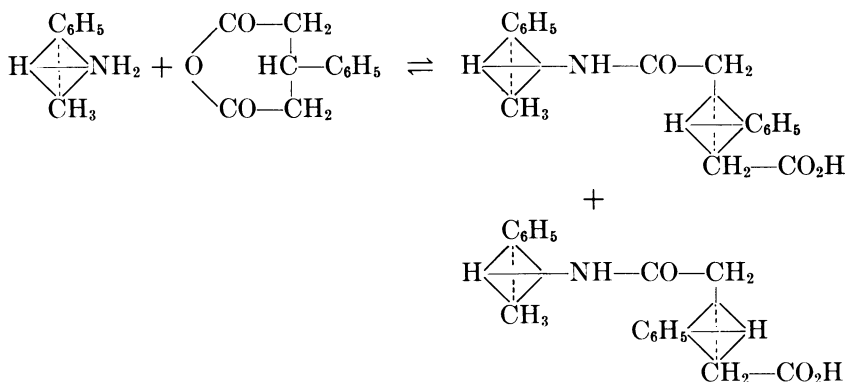
COMMENTS ON A "MESO-CARBON ATOM"

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Schwartz and Carter¹ report a disproportionate yield (60-40 per cent) of two products when (*levo*)- α -methylbenzylamine was reacted with 3-phenylglutaric anhydride, and claim that this demonstrates the stereochemical nonequivalence of the two groups attached to the $C_6H_5(H)C<$ system of the 3-phenylglutaric anhydride. They designate such a substituted carbon a "meso-carbon atom." Actually, Schwartz and Carter have subjected a compound containing an optically active center to an equilibrium reaction in which a new asymmetric center is formed. The products are then diastereoisomers, possessing different chemical energies, and the reverse reaction will set up an equilibrium involving a disproportionate ratio of products, as shown below (the absolute configurations are assumed).



The above type of reaction is well known and is no different in principle from the Kiliani reaction, whereby D-arabinose is converted into disproportionate amounts of D-glucose and D-mannose. The cause of this disproportionation resides in the optically active nature of the initial compound and not in any "stereochemical nonequivalence" of two groups in the optically inactive substance, real as that may be. In the early days of the development of the Van't Hoff-Le Bel theory of the tetrahedral carbon atom, many experimental attempts were made to resolve